Application Note

Energy and Chemicals

Elemental Impurity Analysis of Lithium Ion Battery Anodes using Agilent ICP-MS

Accurate, multi-element determination of low-level contaminants in graphite anode material

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Introduction

Since first becoming commercially available in 1991, rechargeable lithium-ion (Li-ion) batteries (LIBs) have become an integral, even essential, part of modern life. LIBs power everything from smartphones and watches to implantable medical devices, and from electric vehicles (EVs) to the life support systems in NASA astronauts' space suits. Larger scale LIBs are also being utilized for grid-scale storage of the electricity generated by intermittent renewable sources such as wind and solar. LIBs have become ubiquitous due to their combination of high energy density, fast charging capability, uniform (flat) discharge voltage profile, little or no memory effect, low self-discharge rate, good durability, and relatively low cost.

In simple terms, a modern Li-ion battery consists of four components, the anode, cathode, electrolyte, and separator. Several different Li-transition metal alloys (for example, lithium cobalt oxide) and Li salts (including lithium hexafluorophosphate) are used for the cathode material and electrolyte, respectively. But, since 1994, graphite has been used almost exclusively for the anode material in all LIBs (*1*). Graphite—either natural (purified to 99.99% graphite) or synthetic—is the preferred material due to its cost, availability, and excellent charge/discharge characteristics. Other anode materials have been investigated, but none currently matches the overall capability of graphite.

During LIB charging, Li ions are released from the cathode, migrate through the electrolyte, and are stored in the graphite anode in the lithiated graphite compound, LiC_6. During discharge, the reverse process occurs, with Li ions migrating from the anode to the cathode. LIB performance is limited to a large extent by the capacity of the anode graphite crystal lattice to store and release Li ions during the charge/discharge cycle. The anode capacity depends on the morphology and composition of the graphite, and its electrochemical properties are strongly affected by anode dopant and coating elements, as well as contaminants (*2*). As LIB manufacturers strive to develop batteries with higher capacity and faster charging cycles, the performance of the graphite anode is one of the key areas being investigated. As a result, the purity of the graphite anode raw material is being carefully studied.

Most LIB anode graphite is produced and refined in China, and the technique typically used for measuring contaminant elements in graphite is inductively coupled plasma optical emission spectroscopy (ICP-OES) (*3*). The Chinese standard for graphite negative electrode materials for lithium ion battery (GB/T 24533-2019) (*4*) specifies limits for Na, Al, Fe, Co, Cr, Cu, Ni, Zn, Mo, and S. Of these elements, Fe, Cr, Ni, Zn, and Co are grouped and the sum of the concentrations is reported as "Magnetic substance" under the GB standard. In addition, the GB standard has maximum limits for the hazardous heavy metals Cd, Hg, Pb, and Cr(VI)), with ICP-MS specified as a recommended analytical technique.

Advanced battery manufacturers are interested in measuring a wider range of contaminants, some at levels that are below the detection limit of ICP-OES. Researchers are therefore investigating ICP mass spectrometry (ICP-MS), which has detection limits several orders of magnitude lower than ICP-OES, as an alternative analytical technique for characterization of graphite and graphite-based anode materials. ICP-MS provides low detection limits for almost every element, so can be used for characterization of a much wider range of contaminants than just the elements specified in current standard methods. In this work, 45 elements in total were measured in the graphite material by ICP-MS.

Experimental

Instrumentation

The analysis of graphite anode material samples was performed using an Agilent 7850 ICP-MS, which includes the Ultra High Matrix Introduction (UHMI) aerosol dilution system and ORS^4 collision/reaction cell. The 7850 was configured with the standard sample introduction system consisting of a MicroMist nebulizer, Peltier-cooled quartz double-pass spray chamber, and 2.5 mm injector quartz torch. The standard nickel interface cones were used. In the interests of speed and method simplicity, measurement of all elements covering a concentration range from low ng/L (ppt) to high mg/L (ppm) was performed using a single set of ORS^4 He/KED collision mode conditions. If even lower detection levels were the goal, some of the elements measured, such as P, S, and Se, would benefit from alternative cell conditions using enhanced (higher collision energy) He mode, or hydrogen or oxygen reaction gas modes. These modes are optimized for removal or avoidance of intense plasma-based polyatomic interferences. The main instrument operating conditions are shown in Table 1. Sample introduction was performed using an Agilent SPS 4 autosampler, while optimization of the 7850 and run control for the automated analysis sequence was performed using Agilent ICP-MS MassHunter software.

Table 1. Agilent 7850 ICP-MS operating conditions.

Parameters	Value
RF Power (W)	1550
Sampling Depth (mm)	8.0
Nebulizer Gas Flow (L/min)	1.01
UHMI Dilution Gas (L/min)	0.10
Spray Chamber Temperature (°C)	2.0
Lens Tune	Autotune
He Flow Rate (mL/min)	4.3
KED Bias (V)	3

Sample preparation

Two different graphite-based anode material samples sourced from the Li-Ion battery manufacturing industry were purchased. These samples were defined as Sample A and Sample B.

About 1.00 ± 0.01 g of each sample was accurately weighed into a polytetrafluoroethylene (PTFE) microwave digestion vessel. Each sample was digested in 8 mL of aqua regia prepared from ultrapure grade acids, HNO_3 (2 mL) and HCl (6 mL). The sample digests were kept at ambient temperature for 20 minutes before digestion using a Milestone Ethos microwave digestion system. The microwave digestion program is shown in Table 2.

Table 2. Microwave digestion program.

Step	Temperature, °C	Hold Time (minutes)
0	Ambient	Predigestion for 20 minutes
I	150	10
II	160	10
III	180	25
IV	Ambient	Cool to ambient

Once cooled to ambient temperature, the digested solutions were transferred to 50 mL centrifuge tubes and made up to a final volume of 40 mL using de-ionized water. The digests were refrigerated, then centrifuged at 10,000 rpm for 10 minutes at 23 °C, and the supernatant solution was extracted for analysis. All the samples, method blanks, and spiked samples were prepared using the same procedure (Figure 1). For each graphite sample, Sample A and Sample B, six separate sample replicates were prepared.

Calibration standards

Calibration standards for the 45 elements studied in the graphite samples were prepared from Agilent standard solutions: multi-element calibration standard-2A (p/n 8500-6940), multi-element calibration standard-3 (p/n 8500-6948), multi-element calibration standard-4 (p/n 8500-6942), and single element standards for phosphorus (p/n ICP-115) and sulfur (p/n 5190-8529). Calibration standards were prepared in a mix of 5% HNO_3 by volume (v/v) and HCl (present at 10% in calibration standard-3) to stabilize some chemically incompatible elements such as Ag, Sn, Hg, and the PGEs. A mixed acid rinse solution was used, to ensure good control of carry-over of all the elements.

Most of the target analytes (Be, V, Cr, Ga, Ge, As, Se, Rb, Sr, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, Sn, Sb, Te, Cs, Ba, Hf, Re, Ir, Pt, Au, Tl, Pb, U) were calibrated using standards from 0.01 to 20.0 ppb. B and Zn were calibrated using the same standards, in the range from 1.0 to 20.0 ppb. Hg was calibrated separately from 0.005 to 1.0 ppb to ensure low background and chemical stability, while the major elements, Na, Mg, Al, P, S, K, Ca, Mn, Fe, Co, Ni, Cu, were calibrated from 0.01 to 10 ppm.

A mixed internal standard (ISTD) solution was prepared by mixing Agilent single element standards for scandium (Sc) (p/n 5190-8517), terbium (Tb) (p/n 5190-8535), lutetium (Lu) (p/n 5190-8479), and bismuth (Bi) (p/n 5190-8362) in a matrix of 2% HNO_3 (v/v). The ISTD solution (1 mg/L) was mixed with the sample online using the standard ISTD T-connector. Compared to offline addition of the ISTD solution into each sample vial, online addition saves operator time and reduces the potential for errors by eliminating one of the manual sample handling steps.

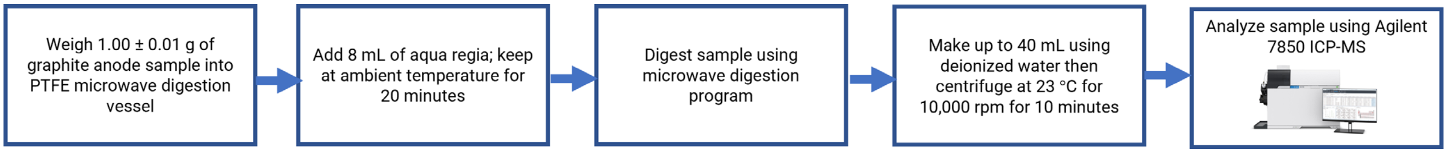

Figure 1. Analytical workflow used for the preparation and ICP-MS analysis of graphite material used in lithium-ion battery anode.

Spiked sample preparation

To test the accuracy of the quantitative method, a spike recovery study was carried out by spiking both the anode material sample digests with elements of known concentrations. From the initial studies, it was observed that graphite Samples A and B contained different levels of the elements of interest. Taking this difference into account, the two anode digest samples were spiked with different analyte concentrations to give spike levels appropriate for the different native concentrations in the digest solutions. The spike recovery samples were prepared and spiked in triplicate for each anode material.

Results and discussion

Detection limits

Instrument detection limits (IDLs) for the 45 elements measured in graphite were calculated as 3 x standard deviation (SD) of the concentration determined in the calibration blank (n=10). Dilution-corrected detection limits were calculated after applying the dilution factor of 40 (1.00 ± 0.01 g of sample, digested and diluted in 40 mL) to give DLs relative to the original solid graphite sample. The measured and dilution corrected DLs are shown in Table 3, together with the linear regression (R) values for the calibration plots. The low DLs demonstrate the suitability of the 7850 ICP-MS for the determination of trace elements, while the R values close to 1 indicate the linear response of the 7850 over a wide concentration range.

Table 3. Calibration coefficients (R), IDLs, and dilution corrected DLs of the 45 elements.

Element	R Value	IDL in Solution (ng/L except elements in bold, µg/L)	Dilution Corrected DL in Solid, µg/kg
9 Be	1.0000	0.76	0.03
11 B	1.0000	130	5.2
23 Na	**0.9999**	**0.1483**	**5.93**
24 Mg	0.9999	60	2.4
27 Al	1.0000	70	2.8
31 P	**1.0000**	**4.36**	**174.4**
34 S	**0.9997**	**33.05**	**1322**
39 K	1.0000	449.9	18
44 Ca	**0.9999**	**3.723**	**148.92**
51 V	0.9999	10.94	0.44
52 Cr	0.9999	1.676	0.07
55 Mn	1.0000	13.22	0.53
56 Fe	1.0000	41.56	1.66
59 Co	0.9999	19	0.76
60 Ni	0.9999	11.06	0.44
63 Cu	0.9999	44.33	1.77
66 Zn	0.9999	76.9	3.08
71 Ga	0.9999	0.6434	0.03
72 Ge	0.9999	3.99	0.16
75 As	0.9999	1.761	0.07
78 Se	0.9999	50.55	2.02
85 Rb	0.9999	1.278	0.05
88 Sr	1.0000	6.853	0.27
90 Zr	1.0000	0.4358	0.02
93 Nb	1.0000	0.475	0.02
95 Mo	1.0000	0.9422	0.04
101 Ru	1.0000	0.1645	0.01
103 Rh	1.0000	1.999	0.08
105 Pd	1.0000	2.099	0.08
107 Ag	0.9995	0.39	0.02
111 Cd	1.0000	0.3225	0.01
118 Sn	1.0000	7.046	0.28
121 Sb	1.0000	1.502	0.06
125 Te	0.9999	4.522	0.18
133 Cs	0.9999	1.781	0.07
137 Ba	1.0000	2.611	0.1
178 Hf	0.9999	2.498	0.1
185 Re	0.9998	0.1567	0.01
193 Ir	1.0000	2.134	0.09
195 Pt	1.0000	1.095	0.04
197 Au	0.9996	7.445	0.3
202 Hg	0.9998	5.773	0.23
205 Tl	1.0000	0.2042	0.01
Pb*	1.0000	5.021	0.2
238 U	1.0000	0.7788	0.03

**Pb was quantified based on the sum of the intensities measured at the three most abundant isotopes, 206, 207, and 208.*

Instrument robustness and internal standard stability

The analytical sequence—comprising digested samples (six digests for each of the two graphite samples), method blanks, quality control (QC) checks, and spike recovery solutions—was analyzed repeatedly over 10 hours. The entire sequence contained more than 200 sample runs in total, with the sample digests containing high acid levels and nominally 2.5% total dissolved solids (TDS). Tb, Lu, and Bi were used as the ISTDs for the analysis of contaminant elements in the graphite anode samples. As shown in Figure 2, the ISTD recoveries remained stable throughout the run, within the ±20% limits indicated by the red dotted lines. The consistent, stable ISTD recoveries show that the robust plasma of the 7850 ICP-MS with UHMI aerosol dilution was able to decompose the matrix effectively, enabling excellent stability to be maintained over the long run. Also, the lack of drift confirms that no significant matrix deposition occurred on the interface during the sequence. The results demonstrate that the 7850 ICP-MS has the robustness and high matrix tolerance for the simple, routine elemental analysis of graphite anode materials.

Quality control check

As a check on the instrument stability and long-term validity of the calibration, QC standards containing 0.10 µg/L of Hg; 1.0 µg/L of Be, B, V, Cr, Ga, Ge, Zn, As, Se, Rb, Sr, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, Sn, Sb, Te, Cs, Ba, Hf, Re, Ir, Pt, Au, Tl, Pb, U, and 1.0 mg/L of Na, Mg, Al, P, S, K, Ca, Mn, Fe, Co, Ni, Cu were analyzed before and after the batch analysis. The drift (% difference) between the measurements was less than 5.0% for all the elements and 1% or less for most elements, as shown in Table 4. This consistency again demonstrates the stability and robustness of the 7850 ICP-MS for routine analysis of graphite-based materials.

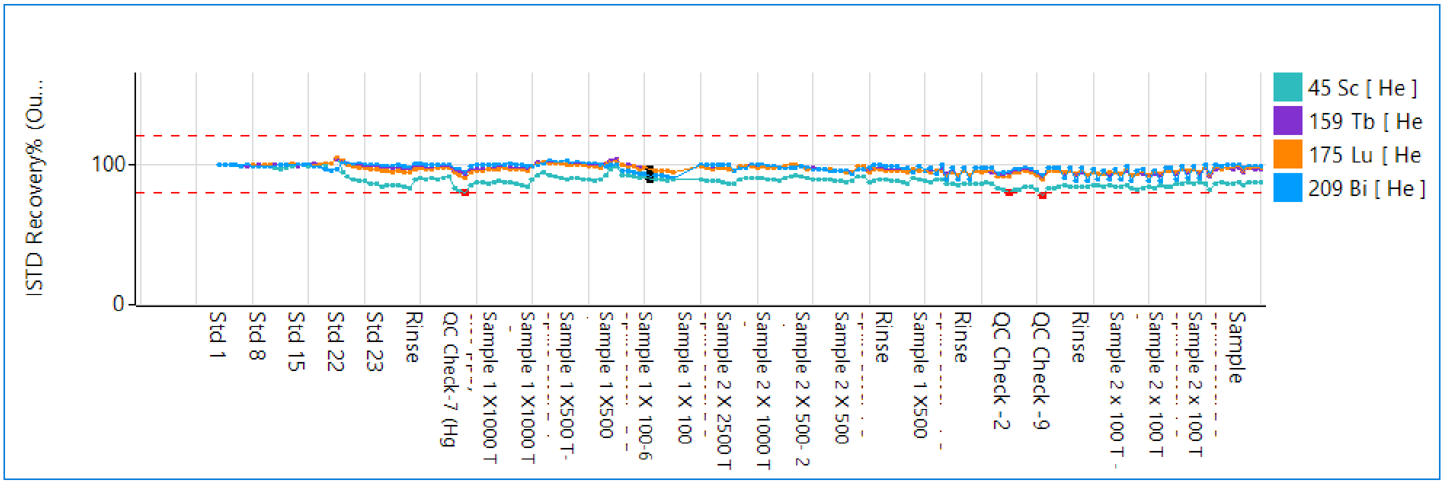

Figure 2. Recovery of ISTD measured over 10 hours (more than 200 acquisitions) using the Agilent 7850 ICP-MS. Due to limited space, not all sample names are shown.

Table 4. Measured concentrations and drift between QC check solutions measured before and after the 10-hour sample analysis run using the Agilent 7850 ICP-MS.

Element	Unit	Concentration in QC Run	Measured Concentration		Drift (%)
			Before Batch Analysis	After Batch Analysis	
9 Be	µg/L	1.00	0.96	0.96	0.14
11 B	µg/L	1.00	1.04	1.00	−4.02
23 Na	mg/L	1.00	0.94	0.95	1.14
24 Mg	mg/L	1.00	0.95	0.97	2.03
27 Al	mg/L	1.00	0.93	0.95	2.33
31 P	mg/L	1.00	0.95	0.97	1.77
34 S	mg/L	1.00	0.98	0.98	0.31
39 K	mg/L	1.00	0.99	1.00	0.69
44 Ca	mg/L	1.00	0.98	0.97	−1.53
51 V	µg/L	1.00	0.93	0.93	0.06
52 Cr	µg/L	1.00	0.99	0.99	0.09
55 Mn	mg/L	1.00	0.94	0.96	1.62
56 Fe	mg/L	1.00	0.94	0.96	1.69
59 Co	mg/L	1.00	0.99	1.00	0.85
60 Ni	mg/L	1.00	1.00	1.01	1.06
63 Cu	mg/L	1.00	1.01	1.02	1.16
66 Zn	µg/L	1.00	0.95	0.93	−2.11
71 Ga	µg/L	1.00	1.01	1.02	0.51
72 Ge	µg/L	1.00	1.05	1.04	−0.99
75 As	µg/L	1.00	1.02	1.02	0.06
78 Se	µg/L	1.00	0.94	0.95	1.67
85 Rb	µg/L	1.00	1.02	1.01	−1.04
88 Sr	µg/L	1.00	1.00	1.00	0.01
90 Zr	µg/L	1.00	1.00	1.01	1.09
93 Nb	µg/L	1.00	1.02	1.02	0.57
95 Mo	µg/L	1.00	1.05	1.04	−0.39
101 Ru	µg/L	1.00	1.05	1.05	0.34
103 Rh	µg/L	1.00	1.03	1.04	0.17
105 Pd	µg/L	1.00	0.99	0.99	0.52
107 Ag	µg/L	1.00	1.03	1.03	0.52
111 Cd	µg/L	1.00	1.06	1.04	−1.64
118 Sn	µg/L	1.00	1.04	1.06	1.57
121 Sb	µg/L	1.00	1.06	1.05	−0.81
125 Te	µg/L	1.00	1.02	1.02	0.02
133 Cs	µg/L	1.00	0.99	1.00	0.95
137 Ba	µg/L	1.00	1.04	1.06	1.50
178 Hf	µg/L	1.00	1.02	1.02	0.63
185 Re	µg/L	1.00	1.05	1.04	−1.38
193 Ir	µg/L	1.00	1.05	1.06	0.55
195 Pt	µg/L	1.00	1.11	1.10	−0.81
197 Au	µg/L	1.00	0.96	1.00	4.50
202 Hg	µg/L	0.10	0.094	0.094	0.47
205 Tl	µg/L	1.00	1.04	1.05	0.41
Pb*	µg/L	1.00	1.07	1.07	0.68
238 U	µg/L	1.00	1.04	1.04	0.22

**Pb was quantified based on the sum of the intensities measured at the three most abundant isotopes, 206, 207, and 208.*

Quantitative batch results

Six separate digests of each of the two graphite anode samples, Sample A and B, were analyzed using the 7850 ICP-MS and the concentrations of 45 contaminant elements were quantified against the multi-element calibrations. The measured results determined in Sample A and B are shown in Table 5 and 6, respectively. The results are corrected for the dilution factor, so are reported in mg/kg in the original solid graphite material. The variation in the quantitative results measured in the six separate digests was excellent, with %RSD of less than 5%.

Table 5. Measured concentrations of 45 elements in six separate digests of graphite Sample A. Results in mg/kg in the original solid sample.

Element	Sample A Replicate Digest							
	I	II	III	IV	V	VI	Average (n=6)	% RSD
9 Be	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-
11 B	0.25	0.23	0.24	0.23	0.25	0.25	0.25	4.8
23 Na	40	40	39	39	39	39	39	0.9
24 Mg	10	10	10	10	10	10	10	0.7
27 Al	144	143	143	144	144	145	144	0.6
31 P	86	83	84	84	85	86	85	1.3
34 S	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-
39 K	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-
44 Ca	22	22	23	21	21	23	22	4.8
51 V	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.9
52 Cr	2.6	2.6	2.6	2.7	2.6	2.6	2.6	0.4
55 Mn	15508	15413	15431	15493	15427	15244	15419	0.6
56 Fe	297	296	295	294	295	295	295	0.3
59 Co	1655	1642	1639	1646	1643	1625	1642	0.6
60 Ni	441	443	439	439	438	438	440	0.5
63 Cu	405	407	405	404	402	405	405	0.4
66Zn	0.70	0.69	0.69	0.70	0.69	0.69	0.69	0.9
71 Ga	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.5
72 Ge	0.17	0.17	0.17	0.17	0.18	0.17	0.17	1.9
75 As	1.4	1.4	1.4	1.4	1.4	1.4	1.4	0.7
78 Se	0.24	0.23	0.23	0.23	0.23	0.23	0.23	1.0
85 Rb	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.6
88 Sr	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.5
90 Zr	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.4
93 Nb	1.1	1.1	1.1	1.1	1.1	1.1	1.1	0.8
95 Mo	0.07	0.07	0.07	0.07	0.07	0.07	0.07	1.3
101 Ru	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-
103 Rh	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-
105 Pd	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-

Table 5 continues on next page

Table 5 continued...

Element	Sample A Replicate Digest							
	I	II	III	IV	V	VI	Average (n=6)	% RSD
107 Ag	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-
111 Cd	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-
118 Sn	4.7	4.7	4.7	4.8	4.7	4.7	4.7	0.5
121 Sb	0.15	0.14	0.14	0.14	0.14	0.14	0.14	0.7
125 Te	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-
133 Cs	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-
137 Ba	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.5
178 Hf	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-
185 Re	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-
193 Ir	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-
195 Pt	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-
197 Au	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-
202 Hg	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-
205 Tl	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-
Pb*	4.3	4.3	4.3	4.4	4.3	4.3	4.3	0.4
238 U	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-

**Pb was quantified based on the sum of the intensities measured at the three most abundant isotopes, 206, 207, and 208.*

Table 6. Measured concentrations of 45 elements in six separate digests of graphite Sample B. Results in mg/kg in the original solid sample.

Element	Sample B Replicate Digest							
	I	II	III	IV	V	VI	Average (n=6)	%RSD
9 Be	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-
11 B	1.5	1.6	1.5	1.6	1.6	1.6	1.6	2.9
23 Na	15	15	15	15	15	15	15	1.3
24 Mg	14	14	14	14	14	14	14	1.4
27 Al	303	318	313	313	315	313	313	1.7
31 P	98	102	102	101	101	101	101	1.5
34 S	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-
39 K	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-
44Ca	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-
51 V	0.06	0.07	0.07	0.06	0.06	0.07	0.07	2.0
52 Cr	0.31	0.32	0.31	0.31	0.31	0.31	0.31	1.4
55Mn	222	230	226	227	225	226	226	1.2
56 Fe	104	108	106	106	105	106	106	1.2
59 Co	15877	15807	15797	15888	15847	15964	15863	0.4
60 Ni	210	219	214	214	213	214	214	1.3
63 Cu	255	264	259	259	257	259	259	1.2
66Zn	2.6	2.7	2.6	2.6	2.6	2.6	2.6	1.4
71 Ga	0.08	0.09	0.09	0.08	0.08	0.08	0.08	3.0
72 Ge	0.06	0.07	0.07	0.07	0.07	0.07	0.07	4.4

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Table 6 continued...

Element	Sample B Replicate Digest							
	I	II	III	IV	V	VI	Average (n=6)	%RSD
75 As	13.9	15.2	14.5	14.6	14.5	14.5	14.5	2.7
78 Se	0.12	0.13	0.13	0.13	0.13	0.13	0.13	2.0
85 Rb	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-
88 Sr	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.2
90 Zr	0.16	0.17	0.16	0.16	0.16	0.16	0.16	0.8
93 Nb	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-
95 Mo	0.04	0.04	0.04	0.04	0.04	0.04	0.04	1.0
101 Ru	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-
103 Rh	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-
105 Pd	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-
107 Ag	0.07	0.07	0.07	0.07	0.07	0.07	0.07	1.3
111 Cd	0.01	0.01	0.01	0.01	0.01	0.01	0.01	2.8
118 Sn	1.3	1.4	1.3	1.3	1.3	1.3	1.3	1.2
121 Sb	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-
125 Te	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-
133 Cs	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-
137 Ba	0.29	0.30	0.29	0.29	0.29	0.29	0.29	1.2
178 Hf	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-
185 Re	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-
193 Ir	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-
195 Pt	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-
197 Au	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-
202 Hg	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-
205 Tl	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-
Pb*	0.71	0.73	0.71	0.71	0.71	0.72	0.72	1.1
238 U	<DL	<DL	<DL	<DL	<DL	<DL	<DL	-

**Pb was quantified based on the sum of the intensities measured at the three most abundant isotopes, 206, 207, and 208.*

Spike recoveries and evaluation of matrix effects

To confirm the accuracy of the quantitative analysis results, a spike recovery study was carried out for each of the two graphite sample digests. The results for Sample A and B are shown in Table 7 and 8, respectively. For all analytes, the spike recoveries (n=3) were within 100 ± 10% with %RSD less than 5%. The excellent recoveries indicate that all elements were unaffected by any matrix effects arising from the graphite sample matrix.

Table 7. Spike recovery accuracy and precision for triplicate preparation of graphite Sample A. All concentrations in µg/L except elements in bold (mg/L).

Elements	Sample A							
	Unspiked Sample Concentration	Spike Concentration	Mean Measured Concentration in Spiked Sample (n=3)	% Recovery				
				Spike replicate I	Spike replicate II	Spike replicate III	Average (n=3)	% RSD
9 Be	<DL	12.5	12.25	97.5	94.7	97.7	96.6	1.7
11 B	6.25	12.5	18.75	97.1	103.9	104.1	101.7	3.9
23 Na	**0.975**	**1.25**	**2.225**	**96.4**	**99.2**	**100.4**	**98.7**	**2.1**
24 Mg	**0.25**	**1.25**	**1.45**	**94.9**	**98.1**	**98.9**	**97.3**	**2.2**
27 Al	**3.6**	**1.25**	**4.8**	**93.2**	**97.0**	**97.6**	**95.9**	**2.5**
31 P	**2.125**	**1.25**	**3.275**	**95.7**	**89.9**	**90.9**	**92.2**	**3.4**
34 S	**<DL**	**1.25**	**1.2**	**94.7**	**95.8**	**96.8**	**95.7**	**1.1**
39 K	**<DL**	**1.25**	**1.2**	**94.7**	**95.8**	**96.8**	**95.7**	**1.1**
44 Ca	**0.55**	**1.25**	**1.725**	**91.7**	**94.7**	**95.3**	**93.9**	**2.0**
51 V	2.75	12.5	16	106.8	105.0	104.5	105.4	1.1
52 Cr	65	12.5	77.5	95.1	95.8	103.2	98.0	4.6
55 Mn	**385.475**	**125**	**511.85**	**95.3**	**104.0**	**103.8**	**101.1**	**4.9**
56 Fe	**7.375**	**1.25**	**8.64**	**98.6**	**102.5**	**103.5**	**101.5**	**2.5**
59 Co	**41.05**	**125**	**173.18**	**103.3**	**106.1**	**107.8**	**105.7**	**2.2**
60 Ni	**11**	**1.25**	**12.32**	**102.6**	**106.4**	**107.5**	**105.5**	**2.4**
63 Cu	**10.125**	**1.25**	**11.46**	**103.6**	**107.5**	**108.4**	**106.5**	**2.4**
66 Zn	17.25	12.5	30	96.3	92.1	97.0	95.2	2.8
71 Ga	27.5	12.5	40	93.5	97.5	91.1	94.0	3.4
72 Ge	4.25	12.5	16.25	95.7	94.3	94.9	94.9	0.7
75 As	35	12.5	47.5	97.9	95.7	94.0	95.9	2.0
78 Se	5.75	12.5	17.25	91.4	92.7	93.7	92.6	1.3
85 Rb	1	12.5	12.25	91.7	91.7	90.9	91.4	0.5
88 Sr	4.25	12.5	15.75	91.7	90.4	91.8	91.3	0.8
90 Zr	8.75	12.5	20.25	92.5	90.7	91.7	91.6	1.0
93 Nb	27.5	12.5	40	102.9	98.4	100.0	100.4	2.3
95 Mo	1.75	12.5	13.5	94.7	93.4	92.8	93.6	1.1
101 Ru	<DL	12.5	11.5	91.7	91.2	91.0	91.3	0.4
103 Rh	<DL	12.5	12.25	97.7	96.8	96.8	97.1	0.5
105 Pd	<DL	12.5	11.75	95.0	93.0	93.4	93.8	1.1
107 Ag	<DL	12.5	12.25	97.5	96.9	96.8	97.1	0.4
111 Cd	<DL	12.5	13	103.6	102.3	103.2	103.0	0.7
118 Sn	117.5	12.5	130	103.8	92.8	90.0	95.6	7.7
121 Sb	3.5	12.5	15.25	94.9	93.8	93.7	94.1	0.7
125 Te	<DL	12.5	11.75	95.5	91.6	94.8	94.0	2.2
133 Cs	<DL	12.5	12.25	90.9	90.4	90.8	90.7	0.3
137 Ba	15	12.5	27.5	96.6	93.8	94.9	95.1	1.5
178 Hf	<DL	12.5	12	94.1	92.8	94.2	93.7	0.8
185 Re	<DL	12.5	11.5	92.8	92.1	92.6	92.5	0.4
193 Ir	<DL	12.5	12.5	99.4	98.8	99.0	99.1	0.3
195 Pt	<DL	12.5	12	95.6	94.8	95.2	95.2	0.5
197 Au	<DL	12.5	12.5	96.9	100.9	102.2	100.0	2.8
202 Hg	<DL	1.8	1.75	92.4	96.1	96.7	95.1	2.5
205 Tl	<DL	12.5	12.5	100.1	99.2	99.7	99.6	0.4
Pb*	107.5	12.5	120	101.4	98.5	100.9	100.3	1.5
238 U	<DL	12.5	11.5	91.5	91.5	92.0	91.7	0.3

**Pb was quantified based on the sum of the intensities measured at the three most abundant isotopes, 206, 207, and 208.*

Table 8. Spike recovery accuracy and precision for triplicate preparation of graphite Sample B. All concentrations in µg/L except elements in bold (mg/L).

Elements	Sample B							
	Unspiked Sample Concentration	Spike Concentration	Mean Measured Concentration in Spiked Sample (n=3)	% Recovery				
				Spike replicate I	Spike replicate II	Spike replicate III	Average (n=3)	% RSD
9 Be	<DL	12.5	12	92.5	94.9	96.1	94.5	1.9
11 B	40	12.5	51	96.5	93	90.8	93.4	3
23 Na	**0.375**	**1.25**	**1.525**	**90.9**	**93.6**	**91.4**	**91.9**	**1.5**
24 Mg	**0.35**	**1.25**	**1.5**	**91.5**	**93.6**	**91.4**	**92.2**	**1.4**
27 Al	**7.825**	**1.25**	**9.15**	**104.8**	**105.4**	**104.5**	**104.9**	**0.5**
31 P	**2.525**	**1.25**	**3.7**	**95**	**94**	**94**	**94.3**	**0.6**
34 S	**<DL**	**1.25**	**1.25**	**98.9**	**101.8**	**99.1**	**99.9**	**1.6**
39 K	**<DL**	**1.25**	**1.175**	**94.8**	**94.2**	**94**	**94.3**	**0.4**
44 Ca	**<DL**	**1.25**	**1.225**	**98.8**	**97.8**	**97.3**	**98**	**0.7**
51 V	1.75	12.5	14.5	103.4	104	103.7	103.7	0.3
52 Cr	7.75	12.5	21.25	106.1	106.5	107	106.5	0.4
55 Mn	**5.65**	**1.25**	**6.925**	**101.9**	**101.8**	**101.8**	**101.9**	**0**
56 Fe	**2.65**	**1.25**	**3.9**	**99.6**	**99.4**	**99.4**	**99.5**	**0.1**
59 Co	**396.575**	**125**	**514.075**	**93.3**	**97.8**	**90.9**	**94**	**3.7**
60 Ni	**5.35**	**1.25**	**6.525**	**95.5**	**90**	**93.2**	**92.9**	**3**
63 Cu	**6.475**	**1.25**	**7.675**	**95.3**	**100.3**	**93.2**	**96.3**	**3.8**
66 Zn	65	12.5	77.5	91.7	92.3	95.6	93.2	2.3
71 Ga	2	12.5	14.5	98.5	98.1	98.8	98.5	0.3
72 Ge	1.75	12.5	14.5	102	103.6	104.5	103.4	1.2
75 As	362.5	125	480	92.5	94.2	92.3	93	1.1
78 Se	3.25	12.5	16.25	103.5	104.6	104.8	104.3	0.7
85 Rb	<DL	12.5	12.5	98.1	98.5	98.3	98.3	0.2
88 Sr	27.5	12.5	40	97.8	96.1	94.6	96.2	1.7
90 Zr	4	12.5	17.25	103.7	105.5	105.3	104.8	0.9
93 Nb	<DL	12.5	13.25	101.7	103.3	102	102.3	0.8
95 Mo	1	12.5	14.25	104.6	106	105.7	105.5	0.7
101 Ru	<DL	12.5	12.75	101.3	102.1	102.2	101.8	0.5
103 Rh	<DL	12.5	12.25	97.4	97.9	98.2	97.8	0.4
105 Pd	<DL	12.5	12	95	95.7	95.6	95.4	0.4
107 Ag	1.75	12.5	14	97.1	97.6	97.3	97.3	0.3
111 Cd	0.01	12.5	13	102.5	102.7	103.1	102.8	0.3
118 Sn	32.5	12.5	45	93.2	95.9	91.6	93.6	2.3
121 Sb	<DL	12.5	13.5	104.8	105.2	104.9	105	0.2
125 Te	<DL	12.5	12.75	103.6	100.3	101.2	101.7	1.7
133 Cs	<DL	12.5	12.25	98.2	98.9	98	98.3	0.5
137 Ba	7.25	12.5	20.25	102.2	104	103.8	103.4	1
178 Hf	<DL	12.5	12.5	100.5	99	97.4	98.9	1.6
185 Re	<DL	12.5	12.5	100.9	99.7	97.4	99.4	1.8
193 Ir	<DL	12.5	12.5	97.5	102.4	102.2	100.7	2.8
195 Pt	<DL	12.5	12.25	99.1	98.5	97.4	98.4	0.9
197 Au	<DL	12.5	13.25	99.8	102.3	100.9	101	1.2
202 Hg	<DL	1.8	1.75	90.9	93.3	92.1	92.1	1.3
205 Tl	<DL	12.5	12.5	100.5	101.1	101.1	100.9	0.3
Pb*	18	12.5	30	100.2	102.3	99.5	100.7	1.5
238 U	<DL	12.5	12	95.2	95.8	95.8	95.6	0.3

**Pb was quantified based on the sum of the intensities measured at the three most abundant isotopes, 206, 207, and 208.*

Conclusion

The Agilent 7850 ICP-MS was used to measure 45 elemental impurities, including the analytes in Chinese standard GB/T 24533-2019, in aqua regia digests of graphite-based anode material used in Li-ion batteries. Low detection limits were achieved in the acid blank, and excellent calibration linearity was obtained for elements covering a wide concentration range. An extended analytical sequence of digested graphite samples, spiked samples, and QC standards was run over a 10-hour period with minimal drift of <1% for most elements and <5% for all elements.

Low levels of most contaminant elements were found in both graphite samples. Some transition metals, notably Mn, Fe, Co, Ni, and Cu were present at high level as a result of the processing of the graphite before and during use as the battery anode. For example, Mn was present at a high concentration (1.54% in the solid graphite) in Sample A, while Co was high (at 1.59%) in Sample B. Many of the elements measured are of interest to manufacturers and must be controlled at low concentrations, as they will affect the electrical and magnetic properties of the graphite material. All the elements—both contaminants and hazardous heavy metals—listed in Chinese Standard GB/T 24533-2019 were determined with good precision (where higher than the DL) and accurate spike recovery. The precision of the analysis across six separate digests of each of the two samples was excellent, with RSDs of around 1% or lower for the six replicate digests. Spike recovery accuracy and precision were also excellent, with mean recoveries for three separate spiked samples being mostly within ±5% of the true spike amount, and with precision around 1% (n=3) for most elements.

The performance evaluation results obtained using the 7850 ICP-MS demonstrate that this instrument can perform the routine analysis of graphite-based LIB anode material. The 7850 offers wide elemental coverage, good accuracy and precision, and much lower detection limits than the existing standard ICP-OES technique. The 7850 ICP-MS therefore offers a viable alternative for LIB manufacturers seeking to develop higher performance graphite anode materials by controlling contaminants at lower levels than can be achieved using ICP-OES.

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